

F 67/5

United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600 S2-81-116 Aug 1981



Project Summary

Physical Properties and Leach Testing of Solidified/Stabilized Flue Gas Cleaning Wastes

KEWASKA PUBLIC LIBRARY

NOV 20 1981

U.S. GOVT. PRINTING
OFFICE

This study examines the effectiveness of five methods of treating flue gas cleaning (FGC) wastes to restrict the release of constituents to contacting waters. Five different FGC sludges were treated using commercially available sludge stabilization technology.

The effects of solidification on several physical and engineering properties of the sludges were determined. These properties were thought to be important in assessing the stabilization techniques, but they were found to be of only moderate predictive value.

The treated and untreated sludges were exposed to leaching conditions in specially designed columns for up to 2 years in a controlled environment, and the resulting leachates were analyzed chemically. Average concentrations of many of the leachate constituents were reduced by most sludge treatment processes, but no single process uniformly reduced the concentrations of all potential pollutants for all sludge types tested.

Two problems occurred regarding the leachate analysis. One was that additional leachable materials were added by means of a reagent during treatment. Thus losses of some constituents were greater than the amount originally present in the sludge. The second problem was that some treatment processes increased the solubility of certain constituents so that they were lost from the treated sludge at higher rates than from the untreated.

Extrapolations of results to field conditions should not be made because

the small sample size (with larger surface/volume ratio) and continuous submersion in a carbon-dioxide-saturated solution produced a rigorous leaching condition that would not be present in actual landfills. Thus wastes would probably be more effectively contained in a field situation. Larger-scale projects are needed for closer duplication of the landfill environment.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Disposing of the power generation industry's waste byproducts is becoming increasingly difficult, expensive, and dangerous to the environment. Existing Federal air pollution control regulations and standards for new, stationary air pollution sources make it virtually impossible to operate a power generation plant using untreated coal (even of moderate sulfur content) without an efficient flue gas desulfurization (FGD) system. Only power plants using very low-sulfur coal are able to operate without flue gas cleaning (FGC) systems.

Most FGC systems now being installed or planned are nonregenerative systems that combine the SO₂ in the stack gas with scrubbing materials to form insoluble calcium sulfite and calcium sulfate, which are collected as FGD sludge. Note that the term "FGC sludge"

EP 1. 89/2.



best copy available

usually refers to a mixture of fly ash, bottom ash, and FGD sludge. Annual production of FGC sludges (50 percent solids) for new power plants burning commonly available grades of coal was estimated to be 20 million tons (wet weight) in 1980; 80 million tons are projected by 1990, and 155 million tons by 1998.

In the past, the predominant method of disposing of these FGC sludges has been to dewater them by ponding and to give them subsequent burial in a landfill. Such disposal methods have a high potential for long-term loss of constituents into adjacent ground and surface waters.

A technology currently being developed and used to address this problem is that of chemical solidification and/or stabilization of the sludge. This treatment attempts to improve the waste's handling characteristics and decrease its potential for leaching undesirable constituents. In this process, additives are combined with the wet sludge and allowed to react with the water and minerals in the sludge to form a solid mass or soil-like material. Most stabilization processes decrease the permeability of the sludge and produce chemical conditions (increased pH) that lower the solubility of sludge constituents.

This study was established to assess the effectiveness of five different methods of treating FGC wastes to restrict the release of constituents to contacting waters. Five different FGC sludges were treated using commercially available sludge stabilization technology. The effects of solidification on several physical and engineering properties of the sludge were determined. The treated and untreated sludges were exposed to leaching conditions in specially designed

columns for up to 2 years in a controlled environment, and the resulting leachates were analyzed chemically. The chemical leaching data were then used to assess the effectiveness of the stabilization processes in containing waste constituents in the FGC sludge tests.

Materials and Methods

Sludges

The three sludges used in this study were selected to be representative of the major scrubber techniques and the major types of coal presently being used: limestone sludge produced with calcium carbonate as a scrubbing reagent, lime sludge produced with calcium hydroxide, and double or dual alkali sludge produced with sodium sulfite. Samples using both eastern (high-sulfur) and western (low-sulfur) coals are used in this study for the lime and double alkali process sludges; only one sample of limestone process FGC sludge using eastern coal is included, however.

All sludges studied here are FGC sludges containing variable amounts of FGC wastes and ash. The major characteristics and chemical composition of the sludges are given in Table 1. All are alkaline, inorganic sludges that are 20 to 30 percent denser than water, have less than 50 percent solids, and contain large amounts of calcium, iron, sulfate, and chloride. The most prevalent heavy metals are chromium, manganese, and zinc. Also present at potentially hazardous but highly variable levels are arsenic, beryllium, cadmium, copper, lead, and nickel. The major source of these elements is the coal burned, but significant amounts can also come from the scrubbing materials and the makeup water.

Stabilization Techniques

The stabilization or fixation processes used in this project generated two types of products: a soil-like material that was highly variable in particle size, and a material capable of being cast into a solid, monolithic block. The solidification procedure used with the first group called for casting the treated sludge into square molds (122 × 122 × 9 cm), covering the molds, curing them for 30 days, breaking the treated samples into smaller pieces (about 5 cm in diameter), and loading them into the leaching columns without further packing. The second group of samples was molded in 7.6-cm-diameter, paraffin-coated tubes 122 cm long. After curing, the tubes were removed, and the resulting cores were used for chemical and physical testing.

The five processes used in this study (designated Processes A, B, E, F, and G) are described here briefly, and their applications to various sludges are noted in Table 1. Process A is a patented procedure that uses fly ash and a lime additive to produce a pozzolan product. Process B is also patented and uses two additives to produce a material of soil-like consistency. Process E uses cement and fly ash (which are readily available commercial materials) as additives to convert waste sludge into a hardened product similar to concrete. Process F mixes a patented additive with a sludge at a pH adjusted to settle the solids in the slurry. The additive is a cementitious product derived from basic, glassy blast furnace slag. Process G is a stabilization technique in which waste sludge is mixed with cement kiln dust (a waste product from the cement industry), and the pH is lowered with either waste sulfuric or phosphoric acid.

Table 1. Major Characteristics, Chemical Constituents, and Stabilization Process Code* of Flue Gas Cleaning Wastes Studied

Waste Description	Sludge ID No.	1978 Production (wet tons)	Solids (%)	Density (kg/m ³)	Sludge Liquor pH	Constituents >10,000 mg/kg (dry)	Constituents 100-10,000 mg/kg (dry)	Constituents 1-100 mg/kg (dry)	Process Designation
Lime Process, Eastern Coal	100	1,160,000	36	1280	10.3	Ca, Fe, SO ₄ , Cl	Cr, Mg, Mn, Zn	As, Be, Cd, Cu, Pb, Ni	A, B, E, F, G
Limestone Process, Eastern Coal	400	1,440,000	36	1280	10.0	Ca, SO ₄ , Cl	Cr, Fe, Mg, Zn	As, Be, Cd, Cu, Pb, Mn, Ni	A, B, E, G
Double Alkali Process, Eastern Coal	500	850,000	44	1330	13.1	Ca, Fe, SO ₄ , Cl	Cr, Mg, Mn, Zn	As, Be, Cd, Cu, Pb, Ni	A, B, E, G
Lime Process, Western Coal	600	2,600,000	20	1120	7.5	Ca, Fe, SO ₄ , Cl	Cr, Mg, Mn, Zn	As, Be, Cd, Cu, Pb, Ni	A, B, E, F, G
Double Alkali Process, Western Coal	1000	600,000	39	1330	12.7	Ca, SO ₄ , Cl	Fe, Mg	Be, Cd, Cr, Cu, Pb, Mn, Ni, Zn	A, B, E, G

*Processes designated by code letter only (see text for generic description of the processes).

Leaching Column Design

The leaching columns used in this study were designed to simulate leaching from sludges buried in an unlined, water-saturated landfill. Plexiglass tubing (152 cm long by 10.2 cm ID) was used to construct the columns (Figure 1), which were approximately 10 liters in volume and covered to prevent dust and air contamination. An inlet port was located 19 cm below the top of the column, providing space for a fluid head of 2.5 cm on top of the sample. The bottoms of the columns were sealed, and a Teflon stopcock was installed at the lower end as a leachate drain. A collecting well was provided by cementing a perforated plate onto the tube 2.5

cm above the stopcock. Movement of sludge into the leachate collection system was retarded with a 7.6-cm layer of 0.64-cm-diameter polypropylene pellets at the bottom of each column. Flow through the column was regulated by the stopcock to maintain a fluid velocity of approximately 1×10^{-5} cm/sec to simulate the flow rate through a raw sludge or fine silt.

Column Loading and Set Up

The treated sludges that were cast into cylinders were placed into the leaching columns, and the space between the sludge and column wall (about 1.3 cm) was filled with polypropylene pellets to create a dispersed flow

of liquid around the sludge samples. The fixed sludges that were not cast into cylinders were taken from the large molds, broken into smaller pieces, and loaded directly into the columns with no pellet packing. The raw sludges were poured into the columns as a slurry.

In all cases, the leaching fluid was back-flooded into each column from the bottom to remove any air spaces. The specimens were maintained in a saturated-flow condition throughout the experiments. All sample columns were set up in triplicate.

The leaching fluid was deionized water saturated with carbon dioxide at pH 4.5 to 5.0. All materials used in the leaching fluid distribution system were either polypropylene or Teflon to minimize any contamination during the testing. The leaching columns were randomly assigned within a system of racks, each of which was fed from a constant head reservoir at one end of the rack. These reservoirs were in turn connected in series to a central reservoir of the leaching fluid in which the carbon dioxide was equilibrated with the fluid.

One column from each triplicate set of treated and untreated sludge columns was selected randomly to be studied with more sensitive and expensive analytic techniques. Performances of the solidification processes were judged by results from this set of priority columns. Data from the other columns were used to confirm the trends and conclusions noted with the priority columns.

Chemical Analyses

Leachate flowed from the columns continuously and was collected in 4.5-liter plastic bottles. At each sampling interval, the pH, conductivity, and volume of the collected leachate were measured, and each sample was split into aliquots of appropriate volume. Each aliquot was preserved using EPA-accepted techniques. All samples were held at 4°C until analyzed.

Parameters selected for analysis included all potential pollutants. High-resolution metal analysis was performed on the priority column for each sludge type, and low-resolution metal analysis was done with the remaining two replicates.

Leachate samples were collected from each column at logarithmic time intervals for at least 2 years, and many of the priority columns were sampled over a longer period. An extensive

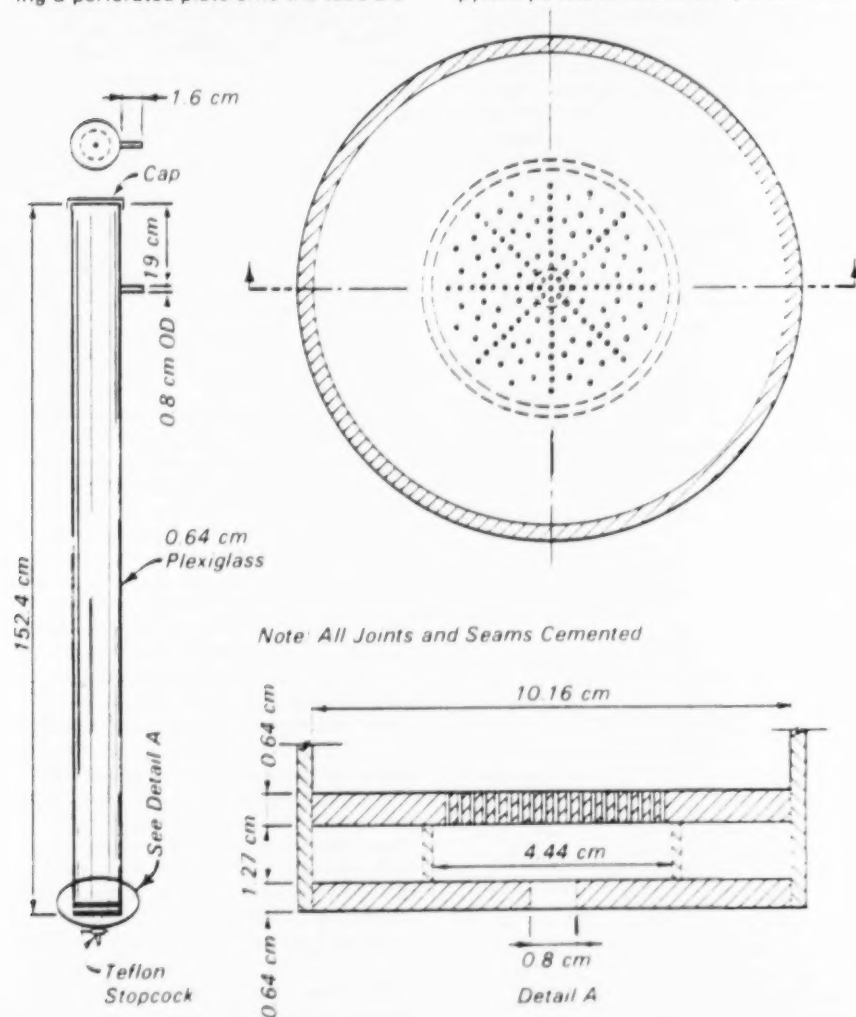


Figure 1. Leaching column design and detail.

quality control program was implemented to ensure precision and accuracy with the analytical system. These efforts were concentrated on metals, since they constituted the major group of pollutants in this project.

Physical and Engineering Properties of FGC Sludges

Test Procedures

Tests commonly used for soil and concrete were performed on the untreated and solidified sludges to determine their physical and engineering properties. The use of these standard tests permitted sludge properties to be compared with those of common materials. Test procedures were selected on the basis of the material's appearance (i.e., soil-like or concrete-like). The testing schedule is shown in Table 2. Standard test procedures were modified as necessary to prevent the alteration of sludge properties during testing and to accommodate nonstandard test specimens.

Sludge Characteristics

The FGC sludges prepared for this study show features typical of this type of sludge: they are made up largely of very small particles with high water content (greater than 50 percent), low bearing capacity, a specific gravity of 2.4 to 3.0, and low permeability (averaging $3 \text{ to } 4 \times 10^{-5} \text{ cm/sec}$). These properties indicate poor handling and dewatering characteristics.

Test Results

Solidification generally produced a material that resembled either soil-

cement mixture or low-strength concrete. This procedure produced no consistent change in specific gravity or water content of the sludges.

Processes A and B yielded materials whose bulk and dry unit weights resembled those of soils (and appeared to be related, as these properties would be in soil). The remaining processes produced materials having very small differences in bulk and dry unit weights (similar to concrete).

Only Process B produced a product that could be subjected to Atterberg limit and compaction tests. Comparison of Atterberg limit tests for untreated and Process-B-treated sludges showed no consistent effect that could be related to the process. Optimum water contents determined from the compaction test were generally higher or equal to values determined for typical soils.

Process B yielded materials that had compressive strengths comparable to those of cohesive or cemented soils. Processes A and G produced materials resembling low-strength soil cement, with two to four times the compressive strengths of samples from Process B. Sludges treated by Processes E and F had compressive strengths in the same range as low-strength concrete.

Sludge samples solidified using Processes B and G have permeabilities resembling those of untreated sludges. Processes A and E decreased the sludge permeabilities to one one-hundredth the value for untreated sludges.

Freeze-thaw and wet-dry testing generally showed that the solidified materials had durability properties similar to soil cement or low-strength concrete. Only sludges solidified by

Process E held up to any degree (all samples withstood wet-dry test cycles and half survived freeze-thaw test cycles).

Physical and engineering tests indicate that solidification processes do not always alter the physical and engineering properties of the sludges in ways that enhance their ability to contain noxious constituents. Testing procedures adapted specifically to sludges and solidified sludges might increase our ability to predict the success of solidification processes.

Results of Leachate Testing

The loss of constituents in the leachate from the experimental columns typically followed one of two distinct patterns, with or without treatment. Those constituents whose concentration in the sludge greatly exceeded their solubilities (e.g., calcium, nickel, lead, and sulfate) were found at relatively constant concentrations in the leachates over the course of the testing. For these constituents, the rate of loss depended on the volume of leachate produced and was independent of the length of time over which the leaching took place. The second leaching pattern was seen in those constituents whose solubilities were large compared with their concentrations in the sludge (e.g., chloride and nitrate). These constituents had very high concentrations in the initial leachate, followed immediately by an asymptotic drop in concentration as the element was depleted from the sludge exposed to the leaching medium. Channelization of leachate flow in the untreated sludge columns greatly increased the rate at which the concentration of the soluble constituents in the leachate fell off, as this process lessened the amount of sludge that came in contact with the leaching medium.

The major pollution problem associated with the untreated FGC sludges is that the leachate from the lime and limestone process is saturated with calcium sulfate (gypsum) and would be expected to remain so for long periods of time. Typically this leachate contains 500 to 600 mg/L calcium and 1200 to 1500 mg/L sulfate. The double alkali process sludges present an added initial problem of extremely high sulfate losses (presumably because of a relatively high proportion of sodium and/or potassium). Leachates containing 35,000 to 40,000 mg/L sulfate were found in early samples from all double alkali columns.

Table 2. Test Schedule for Treated and Untreated FGC Sludges

Type of Test	Untreated Sludges	Solidification Processes				
		A	B	E	F	G
Physical Tests						
Grain-size analysis	X		X		X	
Specific gravity of solids	X	X	X	X	X	X
Water content	X	X	X	X	X	X
Bulk and dry unit weight	X	X	X	X	X	X
Porosity and void ratio	X	X	X	X	X	X
Liquid limit	X		X			
Plastic limit	X		X			
Engineering Tests						
15-blow compaction test			X			
Unconfined compression test		X	X	X	X	X
Permeability test	X	X	X	X	X	X
Freeze-thaw test		X	X	X	X	X
Wet-dry test		X	X	X	X	X

Depletion of the monovalent cations from the double alkali sludges brings about a lowering of the sulfate levels to that found for leachate from other sludge types. Other contaminants in leachates from all untreated FGC sludges that consistently exceeded drinking water standards were arsenic, chromium, and manganese; cadmium and lead exceeded drinking water standards in relatively few leachate samples.

Leaching column tests indicated that the average concentrations of many of the constituents in the leachates collected during this study were reduced by most of the sludge treatment processes; however, no treatment process uniformly reduced the concentration of all constituents in the leachate for all the types of FGC sludges tested. Solidification/stabilization does tend to lower the pollutant potential of FGC sludges to contacting waters. Reduction of the highest concentrations of sludge constituents occurring in the leachate was the most pronounced effect of sludge treatment. When the proportion of dry sludge solids contained in the final solidification/stabilization product is taken into account, the apparent beneficial effect of sludge treatment is reduced, however.

Two possible problems in the treatment processes were identified. In some cases, leachable material appears to have been added by means of the reagent that produces the solidifying or stabilizing reaction. Thus greater amounts of certain constituents were sometimes released from the treated sludge than from the original untreated wastes. In other cases, the treatment process appears to have altered the chemical conditions in the sludge so as to increase the solubility of certain constituents. Consequently, more material was lost from the treated waste than from the equivalent weight of untreated waste.

The small sample size (with larger surface/volume ratio) and continuous submersion in a carbon-dioxide-saturated leaching solution, as used in this study, appear to represent very vigorous leaching conditions. Most landfill operations would allow the use of much larger blocks of treated sludge (with smaller surface/volume ratios) and would undergo only intermittent saturating conditions in the soil. Thus conditions in an actual landfill would be more favorable to the containment of the treated wastes.

Conclusions and Recommendations

The results of this study suggest that solidification/stabilization of FGC wastes may be a feasible method of reducing their pollutant potential in landfilling. A great deal more study is necessary, however, before the behavior of treated FGC sludges under actual field conditions can be adequately understood.

Two years of leaching data indicate that the physical and engineering properties thought to be important in assessing solidification/stabilization techniques are of only moderate predictive value. Specific testing procedures should be developed and standardized to have direct bearing on the ultimate behavior of the final product under actual landfill conditions. But such a step can only be taken with sufficient understanding of the important variables affecting the loss of pollutants from similarly treated materials under actual landfill conditions.

Though the results of small-scale leachate testing can be used with confidence in comparing samples within a small-scale study, extrapolation to field conditions should not be attempted. Most landfilled wastes would have far lower surface-area-to-volume ratios than the small samples used in any

bench-scale testing. Furthermore, the test procedure used here requires the specimens to be constantly immersed in an aggressive leaching medium consisting of water saturated with carbon dioxide. These conditions cause reactions such as hydration of the calcium aluminum silicates in the cement additives and biological activity that may accelerate the release of potential contaminants.

Thus large-scale, controlled tests using treated sludge samples more nearly typical of the surface-to-volume relationship actually encountered in landfill situations are needed for a more realistic estimate of treatment benefits. Intermittent saturation of the treated samples should also be considered in any future testing. In addition, treatment benefits should be calculated on the basis of actual sludge solids incorporated into the treated sludge so that the effects of simple waste dilution can be separated from those of stabilization.

The full report was submitted in fulfillment of Interagency Agreement No. EPA-IAg-D4-0569 by the Waterways Experiment Station, U.S. Army Corps of Engineers, Vicksburg, MS 39180, under the sponsorship of the U.S. Environmental Protection Agency.

This Project Summary was prepared by staff of the Environmental Laboratory, Waterways Experiment Station, U.S. Army Corps of Engineers, Vicksburg, MS 39180.

Robert E. Landreth is the EPA Project Officer (see below).

The complete report, entitled "Physical Properties and Leach Testing of Solidified/Stabilized Flue Gas Cleaning Wastes," (Order No. PB 81-217 036, Cost: \$15.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:
Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
EPA 335



Official Business
Penalty for Private Use \$300

RETURN POSTAGE GUARANTEED

Third-Class
Bulk Rate

